Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at http://about.jstor.org/participate-jstor/individuals/early-journal-content.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact support@jstor.org.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE. — XLVI.

ON THE COMPOSITION OF PETROLEUM.

By Charles F. Mabery.

Presented April 12, 1905. Received April 14, 1905.

THE SULPHUR COMPOUNDS AND UNSATURATED HYDROCARBONS IN CANADIAN PETROLEUM.*

By Charles F. Mabery and William O. Quayle.

In a paper published some time ago by one of us (Mabery) on a preliminary examination of Canadian petroleum (Amer. Chem. Journal, **13**, 89, 1891), it was stated that 225 liters of sulphur oil from Canadian burning oil was in process of distillation for the purpose of separating the individual sulphur constituents. On account of the pressure of other lines of work, study of those distillates was delayed, but it has been resumed at intervals until the results described in this paper were obtained.

On returning to this work it seemed worth while to ascertain first, whether the oil selected really represented constituents of crude petroleum, or whether it consisted to a greater or less extent of decomposition products incident to the process of refining. Since the question of decomposition could be determined in sulphur petroleum from any source, a quantity of crude oil from the Lima (Ohio) field was distilled in vacuo, and the distillate, corresponding to that from which burning oil is prepared, carefully separated, and agitated thoroughly with alcoholic mercuric chloride for the purpose of precipitating the sulphur compounds. The oil was next agitated vigorously with ordinary sulphuric acid, the acid sludge drawn off and diluted with water, carefully avoiding heat so far as possible.

---

* The sulphur derivatives of the hydrocarbons described in this paper are evidently members of a new series, differing essentially in composition, physical properties, and chemical relations from any of the well-known series of sulphur compounds. For this new series I suggest the name Thiophane. C. F. M.

As usual, a dark red oil separated above the solution, but it lacked the heavy sulphurous odor characteristics of sludge as it is ordinarily separated from sulphur petroleum. The odor of this oil resembled that of sludge after the sulphur compounds have been removed, and it showed still greater similarity in its behavior toward bromine, with which it readily united with the evolution of heat, and the formation of an addition product heavier than water precisely similar to the behavior of sludge products. The precipitate with mercuric chloride resembled in all respects the characteristic products which are so useful in separating the sulphur compounds.

As further evidence of the presence of unsaturated hydrocarbons in this oil, a portion of the oil precipitated from sulphuric acid was heated with concentrated hydrobromic acid to 100°, and the product fractioned in vacuo to collect in a smaller limit the bromine addition product. It was not intended to prepare an individual bromine derivative sufficient for analysis, since this would have been impossible with the small amount to be obtained in this manner, but only to be sure that an addition product with hydrobromic acid could be formed. The higher vacuum distillate gave an abundant reaction for bromine after heating with lime, showing that addition of the acid had taken place. The results of these experiments are described in full, that there may be no misapprehension concerning the source of the sulphur compounds and unsaturated hydrocarbons which will be described in this paper. They confirm the results of similar experiments described in the former paper.

In continuing the distillation of the 225 liters of crude sulphur oil with the aid of the apparatus elsewhere described (These Proceedings, **13**, 10), the distillates were carried through entire up to 250° under 50mm., at first within 5°, during four distillations. The lower fractions were then continued within single degree fractions until the lower portions could be distilled under atmosphere-pressure. It was not possible to accomplish in this manner more than a general separation, since all the distillates were mixtures, yet the value of the great amount of tedious labor was shown after the separation of the individual constituents, of which the greater portion distilled at approximately the same temperatures as the original distillates. And although it seemed a great expenditure of effort to distil such a large volume of oil in quantities of ten liters, the capacity of the porcelain still employed, and to continue the distillation of the entire quantity, this seemed to be the only available method for the separation of these peculiar bodies from the crude oil. When first collected, all the fractions were nearly colorless, but on standing they turned dark red, especially those with higher boiling points. The fractions collected below 125°, tension 50mm., were found to be exceedingly unstable. On standing from six months to two years, some of these distillates deposited very dark heavy oils, doubtless formed from unstable unsaturated hydrocarbons, terpenes, or sulphur compounds by polymerization.

In separating the constituents of the vacuum distillates, we followed in general the method described in a former paper (Mabery and Smith, These Proceedings, N. S. **17**, 218). Three or four hundred grams of the oil was shaken in a large flask with an excess of an alcoholic solution of mercuric chloride, which gave a heavy precipitate, crystalline in the lower fractions, a thick viscous mass in the less volatile, and a heavy oily deposit in the vacuum distillates above 160°. There invariably separated above the alcohol a lighter oil, which contained no sulphur, or at most, analysis showed less than one half of one per cent. Upon diluting the alcohol more lighter oil collected, which doubtless has a different composition than the other, since, as will appear later, it showed essentially different properties.

In recovering the sulphur compounds from the mercuric chloride precipitates, after thoroughly washing with alcohol and very volatile gasoline, the precipitate was decomposed by hydric sulphide in presence of a considerable volume of alcohol, the mercuric sulphide separated by filtration, washed with alcohol, and the alcohol largely diluted. For the most part the lighter oil separated, some remaining in suspension, which collected after standing a short time. With all possible care in washing the mercuric chloride precipitate, a single precipitation was never sufficient to remove all the sulphur-free oil. The percentages of sulphur in the individual sulphur compounds invariably came from one to three per cent too low, however long they were fractioned, until they were a second time converted into the mercuric chloride compound and again separated by hydric sulphide. Upon diluting a second time, usually another portion of the sulphur-free oil collected, or remained in suspension, and after sufficient fractioning, the percentage of sulphur then corresponded to the value theoretically required.

It has already been explained that the vacuum fractions of the crude sulphur oil, before the separation of its constituents, is a mixture of an unsaturated hydrocarbon, a sulphur compound, and another hydrocarbon of a series not determined. More attention will be given later to the sulphur-free oils. All the portions selected for the separation of these constituents had previously been fractioned from four to twenty times, for the most part in vacuo, and since the sulphur oil from any particular fraction has corresponded in boiling point to that of the fraction before separation, it has been possible to select from the great number of first fractions those which should give the bodies desired, thereby saving much time and unnecessary labor in searching for the individual constituents.

After the second precipitation from the mercuric chloride compound, a few distillations in vacuo, with the aid of a bead column in a long-necked flask, have been sufficient to bring together, for the most part, within one or two degrees, the sulphur compound desired. For the separation without decomposition of the sulphur oils boiling above 130°, distillation in vacuo has been indispensable. Doubtless exclusion of air, as well as the reduction in boiling points, especially of the higher members, is essential.

The most volatile vacuum distillates 40°–50° were subjected to eight additional distillations within limits of two degrees, and 300 c.c. of these distillates was agitated with an excess of alcoholic mercuric chloride. A part of the oil was immediately converted into a crystalline precipitate, and the sulphur-free oil, which formed the greater part of the oil taken, remained entirely in solution and was separated by dilution. After decantation of the alcoholic solution, the crystalline precipitate was well washed with alcohol and light gasoline, and decomposed by hydric sulphide in presence of alcohol.

For complete removal of the sulphur-free oil the mercuric chloride compound was again formed, washed, and the sulphur oil separated by hydric sulphide. Unfortunately, the larger portion of the sulphur oil was accidentally lost, but the remainder was fractioned, so far as possible, until finally it showed a tendency to collect at 125°–130°.

The percentage of sulphur found in this product was 27.12; required for the sulphur compound $C_6H_{12}S$, 27.60. The crystalline condition of this substance is characteristic of the alkyl sulphides; but all the sulphur bodies we have separated from petroleum are viscous oils that could not be solidified, except the more volatile sulphur compounds such as were separated from Ohio petroleum, which were crystalline.

The following series of sulphur compounds which have been identified by analysis, and shown to have the composition of the general formula $C_nH_{2n}S$, do not represent any series known. They are not members of the ethylene sulphide series, as shown by their reactions and very high specific gravity. In empirical composition they correspond to hydrothiophenes, which have not been synthetically prepared.

HEPTYL THIOPHANE.

Fraction 158°–160° (At. Pres.), $C_7H_{14}S$.

The heptyl sulphur compound was identified in the vacuum distillate 71°–73°, 50 mm., seventh distillation. After precipitation with alcoholic mercuric chloride, and thorough washing with alcohol and light gasoline, the thick viscous oil was decomposed with hydric sulphide in the presence of alcohol. The oil that separated on dilution of the alcohol was fractioned in vacuo until it distilled at 74°–76° under 50 mm., and at 158°–160°, 750 mm. A determination of its specific gravity at 20° gave 0.8878. Analysis gave percentages of carbon, hydrogen, and sulphur required for the formula $C_7H_{14}S$. Carbon and hydrogen were determined by combustion in plumbic chromate, the sulphur by combustion in oxygen.

I. 0.1749 gram of the oil gave 0.4141 gram CO_2, and 0.1748 gram H_2O.
II. 0.1666 gram of the oil gave 0.3071 gram BaO_4.

	Calculated for $C_7H_{14}S$.	Found. I	II
C	64.63	64.59	
H	10.76	11.18	
S	24.61		25.31

OCTYL THIOPHANE.

Fraction 167°–169° (At. Pres.), $C_8H_{16}S$.

For the separation of the next sulphur homologue the large quantity of distillate was selected that collected at 79°–81°, 50 mm., after the seventh distillation. 100 c.c. of this, with the treatment described above, yielded 20 c.c. of the sulphur compound, that distilled constant in vacuo at 81°–83°, 50 mm., and at 167°–169° under atmospheric pressure. The specific gravity of this oil was found to be 0.8929 at 20°. Its composition was shown by the following analyses:

I. 0.1666 gram of the oil gave 0.4057 gram CO_2, and 0.1671 gram H_2O.
II. 0.1391 gram of the oil gave 0.2282 gram $BaSO_4$.

	Calculated for $C_8H_{16}S$.	Found. I.	II.
C	66.67	66.46	
H	11.11	11.22	
S	21.22		22.53

ISOOCTYL THIOPHANE.

Fraction 183°-185° (At. Pres.), $C_8H_{16}S$.

A large amount of distillate collected at 97°-99°, 50mm., at the end of the seventh distillation, that gave by analysis the same empirical formula as the sulphur compound previously described. The term isooctyl is applied to this compound to distinguish it from its isomer. Upon treatment with mercuric chloride and second precipitation, a large amount of sulphur-free oil collected on dilution of the alcohol, and analysis showed that this constituent was completely removed by the second treatment. After fractioning in vacuo this product collected to the extent of 15 c.c. at 94°-96°, 50 mm., and distilled with some decomposition at 183°-185°, atmospheric pressure. Specific gravity at 20°, 0.8937.

This oil gave the required percentages of carbon, hydrogen, and sulphur for the formula $C_8H_{16}S$.

I. 0.1458 gram of the oil gave 0.3592 gram CO_2, and 0.1470 gram H_2O.
II. 0.1561 gram of the oil gave 0.3814 gram CO_2, and 0.1575 gram H_2O.
III. 0.2670 gram of the oil gave 0.4183 gram $BaSO_4$.

	Calculated for $C_8H_{16}S$	Found. I.	II.	III
C	66.67	67.19	66.16	
H	11.11	11.27	11.29	
S	22.22			21.52

It will be observed that the last two compounds have the same empirical composition, but differ by 16° or more in boiling points, and differ also in specific gravity. It will also be observed that they agree closely in boiling points with butyl and isobutyl sulphides; but they differ widely from the latter in specific gravity: butyl sulphide, 0.8523 at 0°: isobutyl sulphide, 0.8363 at 10°, and in other properties.

NONYL THIOPHANE.

Fraction 139°-195° (At. Pres.), $C_9H_{18}S$.

A portion of the distillate that collected in considerable quantity at 106°-108°, 50 mm., was treated in the same manner as previously described with two precipitations for the separation of the sulphur compound. The product was fractioned in vacuo until it collected for the most part at 106°-108°, 50 mm. Under atmospheric pressure it boiled at 193°-195°, and gave as its specific gravity at 20°, 0.8997. On analysis it gave percentages of carbon, hydrogen, and sulphur required for the formula $C_9H_{18}S$.

I. 0.1927 gram of the oil gave 0.4852 gram CO_2, and 0.2033 gram H_2O.
II. 0.1547 gram of the oil gave 0.2210 gram $BaSO_4$.

	Calculated for $C_9H_{18}S$.	Found. I.	II.
C	68.35	68.68	
H	11.40	11.80	
S	20.25		19.62

DECYL THIOPHANE.

Fraction 207°-209°, (At. Pres.), $C_{10}H_{20}S$.

From the vacuum distillate 114°-115°, 50 mm., after the seventh distillation, a sulphur oil was prepared by two precipitations with mercuric chloride, that collected after fractioning some time in vacuo for the most part at 114°-116°, 50 mm. Under a tension of 750 mm., it distilled at 207°-209°, and gave as its specific gravity at 20°, 0.9074. The results of analysis correspond to the formula $C_{10}H_{20}S$.

I. 0.2323 gram of oil gave 0.5904 gram CO_2, and 0.2453 gram H_2O.
II. 0.1981 gram of the oil gave 0.5078 gram CO_2, and 0.2094 gram H_2O.
III. 0.1654 gram of the oil gave 0.2240 gram $BaSO_4$.
IV. 0.1760 gram of the oil gave 0.2407 gram $BaSO_4$.

	Calculated for $C_{10}H_{20}S$.	I.	II.	Found. III.	IV.
C	69.77	69.33	69.92		
H	11.62	11.32	11.82		
S	18.60			18.59	18.78

UNDECYL THIOPHANE.

Fraction 128°-130°, 50 mm., $C_{11}H_{22}S$.

The vacuum distillate 135°-145°, 50 mm., was selected for the separation of the next homologous sulphur compound. A thick tarry mass was formed by precipitation with mercuric chloride, which gave the pure sulphur oil by a second precipitation. The viscosity of the compounds with mercuric chloride was found to increase with increase in molecular weights of the sulphur oils. 300 grams of the first distillate 135°-145°, fourth distillation, gave, after the second precipitation with mercuric chloride, 122 grams insoluble in alcohol, 60 grams in the alcoholic solution, and 84 grams of the sulphur oil. Without further purification, the latter gave 16.08 per cent sulphur. After continued fractioning in vacuo the sulphur oil collected for the most part at 128°–130°, 50 mm., and on analysis it gave the percentages of carbon, hydrogen, and sulphur required for the formula $C_{11}H_{22}S$.

I. 0.1793 gram of the oil gave 0.4669 gram CO_2, and 0.1896 gram H_2O.
II. 0.2064 gram of the oil gave 0.5334 gram CO_2, and 0.2122 gram H_2O.
III. 0.1921 gram of the oil gave 0.2411 gram $BaSO_4$.

	Calculated for $C_{11}H_{22}S$.	Found. I.	II.	III.
C	70.98	71.01	70.71	
H	11.82	11.82	11.50	
S	17.20			17.24

The specific gravity of this sulphur oil was found to be 0.9147 at 20°. Particular attention was given to the purification of this product to be certain of the series as shown by the most careful analysis. In addition to the determinations given above that demonstrate its composition, the following additional analyses were made of different preparations: carbon found, 70.73, 70.74; hydrogen in the same combustions, 11.48, 11.95; sulphur, 17.28, 17.05, 17.10.

The portions of the original sludge oil, called sulphur-free oils to distinguish them from the sulphur oils, have contained from 0.1 to 0.3 per cent of sulphur, and it has been assumed that the small proportion of sulphur indicated a little of the sulphur compound not precipitated by mercuric chloride. That the part collecting above the alcohol after precipitation is a different product from the part remaining in solution in alcohol is shown by the difference in specific gravity. For example, the distillate 136°–145° from which the oil $C_{11}H_{22}S$ was obtained gave an oil insoluble in alcohol with a specific gravity 0.8412; but the specific gravity of the portion in solution was found to be 0.8107. Similar differences appeared in oils associated with other thiophanes. Since the specific gravity of any one of the principal hydrocarbons in Canadian petroleum corresponding in boiling point with these bodies is smaller than the specific gravity of the sulphur oils, and since hydrocarbons are sparingly soluble in sulphuric acid and alcohol, the bodies under examination cannot be the principal petroleum hydrocarbons. Then the odors of both the substances soluble and insoluble in alcohol are unlike that of any of the hydrocarbons, — very pungent, resembling the terpenes. Further study will be necessary to identify these peculiar bodies.

QUATDECYL THIOPHANE.

Fraction 266°–268° (At. Pres.), $C_{14}H_{28}S$.

This sulphur oil was separated from the distillate 160°–170°, fourth distillation, 50 mm. After the second precipitation and decomposition by hydric sulphide, 400 grams of the sludge distillate gave 75 c.c. of a yellow oil that collected for the greater part at 168°–170°, 50 mm., after extended fractioning. It collected at 266°–268° under 750 mm., and gave percentages by analysis required for the formula $C_{14}H_{28}S$. Its specific gravity at 20° was found to be 0.9208.

I. 0.1859 gram of the oil gave 0.5010 gram CO_2, and 0.2109 gram H_2O.
II. 0.2290 gram of the oil gave 0.2336 gram $BaSO_4$.

	Required for $C_{14}H_{28}S$.	Found. I.	II.
C	73.68	73.52	
H	12.28	12.69	
S	14.04		14.02

SEXDECYL THIOPHANE.

Fraction 283°–285° (At. Pres.), $C_{16}H_{32}S$.

From 400 c.c. of the first vacuum distillate 170°–180°, 50 mm., after the second precipitation with mercuric chloride and long-continued distillation, 28.5 grams of the sulphur oil collected at 184°–186°, which distilled with some decomposition at 283°–285°, under 750 mm. Analysis gave values required for the formula $C_{16}H_{32}S$. Its specific gravity was found to be 0.9222.

I. 0.2148 gram of the oil gave 0.5934 gram CO_2, and 0.2380 gram H_2O.
II. 0.1850 gram of the oil gave 0.1683 gram $BaSO_4$.

	Calculated for $C_{16}H_{32}S$.	Found. I.	II.
C	75.00	75.36	
H	12.50	12.40	
S	12.50		12.49

OCTODECYL THIOPHANE.

Fraction 290°–295° (At. Pres.), $C_{18}H_{36}S$.

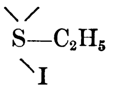
From 350 grams of the vacuum distillate 190°–210°, 50 mm., alcoholic mercuric chloride gave a very thick viscous precipitate, from which was obtained after the second precipitation 50 grams of a dark-colored oil that collected after continued distillation in vacuo, nearly colorless, for the most part at 198°–202°. Under atmospheric pressure this oil distilled with some decomposition at 290°–295°, specific gravity at 20°, 0.9235. The values obtained by analysis corresponded to the formula $C_{18}H_{36}S$.

I. 0.2005 gram of the oil gave 0.5602 gram CO_2, and 0.2214 gram H_2O.
II. 0.1937 gram of the oil gave 0.1634 gram $BaSO_4$.
III. 0.2011 gram of the oil gave 0.1636 gram $BaSO_4$.

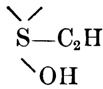
	Calculated for $C_{18}H_{36}S$.	Found. I.	 II.	 III.
C	76.06	76.22		
H	12.67	12.35		
S	11.27		11.57	11.18

We have made no attempts toward the separation of sulphur compounds with higher molecular weights, but there is no doubt that higher homologues are contained in the less volatile distillates which we have separated from the original oil. It is probable that intermediary members of this series are contained in the distillates examined, and that they might be identified in larger quantities of material.

As has been shown in the method of preparation, the thiophanes combine readily with alcoholic mercuric chloride to form viscous oils. They also form addition products with chlorplatinic acid, which are heavy viscous oils. When heated in a sealed tube with ethyl iodide, addition products are formed which crystallize in small prisms, — $C_nH_{2n}S$, C_2H_5I. These addition products form alkaline hydrates when warmed with silver oxide and water:



$$\underset{\diagdown I}{\overset{\diagdown\diagup}{S}}{-}C_2H_5$$



$$\underset{\diagdown OH}{\overset{\diagdown\diagup}{S}}{-}C_2H_5$$

Bromine exerts a characteristic action on these sulphur compounds. Immediately when they come in contact, combination follows with almost explosive violence, and copious evolution of hydrobromic acid in equivalent amounts to the bromine added. It is wholly unlike the behavior of unsaturated hydrocarbons with bromine. Probably part of the bromine combines with the sulphur, but the evolution of hydrobromic acid begins immediately, doubtless due to the ready replacement of the methylene hydrogen atoms.

The thiophanes still further resemble the well-known series of sulphur derivatives in their behavior toward oxidation. The formation and properties of the sulphones will be described later.

In addition to the analytical data that establish the composition of the thiophanes, we have determined their indices of refraction, and the corresponding molecular refraction verifies the formulas given by analysis.

INDICES OF REFRACTION OF THE THIOPHANES.

Many attempts were made to determine the molecular weights of the sulphur compounds in Canadian petroleum with different solvents, but no concordant values could be obtained, even with the same substance and the same solvent.

Better success, however, was reached in ascertaining the indices of refraction. But since the values for sulphur in organic compounds have not been determined with the same certainty as in the case of carbon, hydrogen, and oxygen, some attention was given to verifying this constant.

The index of refraction found by Nasini for ethyl sulphide was 1.44233; for ethyl mercaptan, 1.43055; and for ethyl disulphide, 1.50633.

Assigning the accepted values to carbon and hydrogen, the calculated value for sulphur becomes, for ethyl sulphide, 7.98; for ethyl mercaptan, 7.81; and for ethyl sulphide, 8.03. In determining the value of sulphur in ethyl mercaptan, we found the angle to be 49° 24′, which corresponds to the index 1.4323, and the calculated value for sulphur is 7.89.

Isobutyl sulphide gave us 1.4585 as its index of refraction, calculated from the observed angle 44° 57′; the corresponding molecular refraction is 46.85. Assigning the accepted values to carbon and hydrogen, the difference is the value of sulphur, 7.98, the same as the value calculated from Nasini's index of ethyl sulphide.

The index assigned to thiophen is 1.5268, which gives as its molecular refraction, 24.12, leaving a value for sulphur 6.53. Thiophen is assumed to have two sets of double bonds. The petroleum sulphur compounds under consideration, although doubtless possessing a ring structure, apparently do not contain carbon atoms connected by double linkage. We have therefore considered it safe to use the value 7.98 for sulphur, and the following molecular refraction for the petroleum sulphur compounds were calculated on the basis of this value.

Heptyl Thiophane.

The fraction 74°–76°, 50mm., which proved to contain heptyl thiophane, gave as its index of refraction 1.468, corresponding to the following molecular refraction:

Calculated for $C_7H_{14}S$.	Found.
40.15	40.82

Octyl Thiophane.

From the fraction 83°–85°, 50mm., was separated octyl thiophane. Its index of refraction was found to be 1.4860, and its molecular refraction:

Calculated for $C_8H_{16}S$.	Found.
44.75	44.91

Nonyl Thiophane.

Nonyl thiophane was found to be the principal constituent of the fraction 106°–108°, 50mm. It gave as its index of refraction 1.4746, from which was calculated its molecular refraction:

Calculated for $C_9H_{18}S$.	Found.
49.35	49.50

Decyl Thiophane, $C_{10}H_{20}S$.

The index of refraction of the distillate 114°–116°, from which was separated decyl thiophane, we found to be 1.4766. Its molecular refraction was calculated as follows:

Calculated for $C_{10}H_{20}S$.	Found.
53.94	53.60

Undecyl Thiophane.

Undecyl thiophane was found in the fraction 130°–135°, 50mm. We found its index of refraction to be 1.480, and its molecular refraction:

Calculated for $C_{11}H_{22}S$.	Found.
58.54	58.53

QUATDECYL THIOPHANE, $C_{14}H_{28}S$.

The fraction 168°–170° gave quatdecyl thiophane. Its index of refraction, 1.4892, corresponded to the molecular refraction:

Calculated for $C_{14}H_{28}S$.	Found.
72.33	71.61

SEXDECYL THIOPHANE.

This sulphur body was found in the fraction 184°–186°, 50mm. Its index of refraction proved to be 1.4903, from which its molecular refraction was calculated:

Calculated for $C_{16}H_{32}S$.	Found.
81.52	80.44

The index of refraction of octodecyl thiophane was found to be 1.4977, but the molecular refraction calculated from this value and its specific gravity 0.9625 at 20° gave a value different by four units from the calculated molecular refraction.

OXIDATION PRODUCTS OF THE THIOPHANES.

Appreciating the importance of oxidation products in ascertaining the composition of the thiophanes, we have tried very thoroughly the action of oxidation agents, nitric acid, chromic acid, and potassium permanganate. These sulphur bodies absorb oxygen with great readiness, and the reaction must be carefully controlled to prevent ultimate oxidation to sulphuric acid. It was not found possible to limit the oxidation to the formation of the sulphoxide, since the sulphone seems to be the more stable condition. Nitric acid readily oxidizes the sulphur with an extremely violent reaction, but apparently also forms nitro-derivatives, since the products contain nitrogen.

Chromic acid oxidizes the sulphur readily, with some danger that the reaction proceeds to ultimate oxidation. Potassium permanganate in either alkaline or acid solution readily effects the change with little danger of the formation of sulphuric acid. After careful study of the conditions, it was found that the largest yield of oxidation product was obtained by adding slowly to the oil one and a half times the calculated weight of permanganate dissolved in thirty times its weight of water and keeping the solution cold. With efficient cooling, the permanganate can be added as rapidly as it is decolorized. After the reaction was complete the precipitated manganic oxide was filtered and the solution distilled with steam, which carried over any unoxidized sulphur compound, leaving behind the oxidation product. When carefully conducted the solution shows no sulphuric acid. From the residue of the steam distillation the oxidation product was extracted with ether and the ether evaporated, leaving a thick heavy oil, which increased in viscosity with increase in molecular weight. In several instances we dissolved the precipitated manganic oxide by saturating with sulphurous oxide and extracted with ether. When the oxidation is complete this is the easier method; but distillation with steam insures the removal of any decomposition products.

The action of oxidizing agents showed a wide difference in deportment between the sulphur compounds from Canadian petroleum and sulphides synthetically prepared. For example, synthetic isoamylsulphide allowed to stand with concentrated nitric acid showed vigorous reaction only after several minutes with evolution of heat. After the reaction ceased heat was applied and water added. The oxidation product collected above the water and partly dissolved. Only a trace of sulphuric acid was found in the solution. On treating the sulphur compounds from Canadian petroleum in the same manner, the reaction was much more vigorous, with immediate evolution of heat. The product formed a thick oil heavier than water, and much sulphuric acid was formed. But the oxidized oil contained much sulphur, showing that it consisted in part of an oxidized sulphur compound. This difference in the action of nitric acid is pretty conclusive proof that the sulphur compounds under consideration are not alkyl sulphides, nor, indeed, members of any other well-known series. It is in accordance with the observation that the hydro-ring compounds, the methylenes, are less stable toward reagents than the aromatic or paraffine compounds.

Hexyl Thiophane Sulphone.

The presence of hexyl thiophane was indicated in the fraction 125°–130° atmospheric pressure, although it was not separated in a pure form. In attempting to prepare the sulphone, the fraction 55°–57°, 50 mm., was treated as described above with potassium permanganate. Oxidation was rapid, even when cooled to 0°. In this instance, after dissolving the manganic oxide in sulphurous acid, the solution was evaporated to dryness and the residue extracted with anhydrous ether. Evaporation of the ether left a thick viscous oil with a sweetish taste and odor, and with no reaction for sulphuric acid. While the analytical values obtained indicated that the hexyl compound was contaminated with a higher homologue, it is evident that hexyl thiophane was the principal constituent.

The values given by analysis were as follows:

C, 49.39; H, 8.47; S, 19.02. Required for $C_6H_{12}SO_2$: C, 48.64; H, 8.11; S, 21.62.

HEPTYL THIOPHANE SULPHONE, $C_7H_{14}SO_2$.

The oxidation of heptyl thiophane was conducted as described above. After neutralizing with sodium carbonate and evaporating to dryness, the residue was extracted with anhydrous ether. No sulphuric acid was formed by the oxidation. The following results were obtained by analysis of this product:

I. 0.1992 gram of the substance gave 0.3801 gram CO_2, and 0.1531 gram H_2O.

II. 0.1628 gram of the substance gave 0.2279 gram $BaSO_4$.

	Calculated for $C_7H_{14}SO_2$.	Found.	
		I.	II.
C	51.86	52.05	
H	8.64	8.59	
S	19.75		19.23

This sulphone formed a very thick heavy oil. Its specific gravity was found to be 1.1138 at 20°.

OCTYL THIOPHANE SULPHONE, $C_8H_{16}SO_2$.

50 grams of the fraction 87°–89° identified as octyl thiophane was oxidized carefully at freezing temperature. After dissolving the manganic oxide, and distilling with steam, 36 grams of a heavy oil separated with no formation of sulphuric acid. After neutralizing with sodium carbonate, evaporating to dryness, and extracting with ether, this oil gave as its specific gravity at 20°, 1.1142. Its composition was shown by analysis.

I. 0.1697 grams of the substance gave 0.3385 gram CO_2, and 0.1368 gram H_2O.

II. 0.2038 gram of the substance gave 0.2702 gram $BaSO_4$.

	Calculated for $C_8H_{16}SO_2$.	Found.	
		I.	II.
C	54.55	54.41	
H	9.11	9.01	
S	18.18		18.21

NONYL THIOPHANE SULPHONE, $C_9H_{18}SO_2$.

For oxidation of the nonyl sulphur compound, the fraction 106°–108°, 50 mm., was selected. In the first half of the oxidation the potassium permanganate was added slowly in a bath of ice and salt. The reaction was completed at ordinary temperatures, and it proceeded much more slowly toward the end. The required amount of permanganate was consumed in four days, and no sulphuric acid was formed. In all these oxidations, doubtless sulphonic acids were formed to some extent, but their removal was insured by neutralizing with sodium hydrate and extraction of the evaporated residue with anhydrous ether. The specific gravity of the nonyl sulphone was found to be 1.1161 at 20°. Its composition was shown by analysis.

I. 0.1867 gram of the substance gave 0.3874 gram CO_2, and 0.1509 gram H_2O.

II. 8.1679 gram of the substance gave 0.2071 gram $BaSO_4$.

	Calculated for $C_9H_{18}SO_2$.	Found.	
		I.	II.
C	56.83	56.61	
H	9.47	9.04	
S	16.84		16.93

UNDECYL THIOPHANE SULPHONE, $C_{11}H_{22}SO_2$.

We were unable to isolate an oxidation product which corresponded closely in composition to decyl thiophane sulphone from the original fraction, and the amount of the thiophane isolated was not sufficient for oxidation.

Undecyl thiophane was prepared from the undecyl thiophane separated from the fraction 129°–131°, 50 mm. 7.8 grams of the thiophane gave 5 grams of the oxidation product. The heavy oil left after distillation with steam had a pleasant sweetish odor; its specific gravity was found to be 1.1126 at 20°. The following results were given by analysis:

I. 0.1903 gram of the substance gave 0.4176 gram CO_2, and 0.1621 grams H_2O.

II. 0.1470 gram of the substance gave 0.1579 gram $BaSO_4$.

	Calculated for $C_{11}H_{22}SO_2$.	Found. I.	II.
C	60.54	59.84	
H	10.09	9.53	
S	14.68		14.75

DODECYL THIOPHANE SULPHONE, $C_{12}H_{24}SO_2$.

After treating 7 grams of the distillate 142°–144°, 50 mm., with 9 grams potassium permanganate, the proportions found most suitable, there still remained a slight odor of the thiophane which was completely removed by distillation with steam. The residual oil that remained after extraction of the steam residue with ether gave as its specific gravity at 20°, 1.1372. Its composition was established by analysis.

I. 0.1533 gram of the substance gave 0.3483 gram CO_2, and 0.1402 gram H_2O.

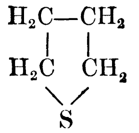
II. 0.1645 gram of the substance gave 0.1554 gram $BaSO_4$.

	Calculated for $C_{12}H_{24}SO_2$.	Found. I.	II.
C	62.07	61.98	
H	10.35	10.23	
S	13.79		12.91

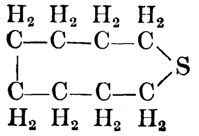
The sulphur compounds in Canadian petroleum have been shown to belong to a series C_nH_{2n}. Their structure must be explained either as unsaturated, like the ethylene sulphides, or by a ring arrangement. That these bodies are not of the ethylene series is shown by the facts that the ethylene sulphides are solids, and that they absorb bromine without evolution of hydrobromic acid. The petroleum sulphur compounds have a very high specific gravity, and they evolve hydrobromic acid copiously when treated with bromine. They resemble the well-known series of sulphur compounds in forming addition products with mercuric chloride, in the formation of sulphones, the formation of addition products with alkyl iodides and alkaline hydrates.

In a former paper by Mabery and Smith it was shown that the sulphur compounds in petroleum are not mercaptans nor thiophenes. The series separated by Mabery and Smith from Ohio petroleum formed crystalline addition products with alcoholic mercuric chloride, and the sulphur oils themselves resembled the alkyl sulphides. But the series contained in the portions of Canadian petroleum with higher boiling points are not alkyl sulphides, mercaptans, thiophenes, nor ethylene sulphides. Their high specific gravity show that they belong to a new series. The hydro-condition of the constituents of Pennsylvania, Ohio, Canadian, Texas, and California petroleum corresponding to the series C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, etc., has been described in former papers, and the proportions of these series are indicated by the differences in specific gravity. Canadian petroleum is composed for the most part of the series of hydrocarbons poorer in hydrogen. Other constituents of petroleum partake of a similar hydro-condition. The nitrogen compounds, for example, in California petroleum, are tetrahydro- and octohydro-bodies, with structure resembling the hydrochinolines.

Empirically the thiophanes are hydrothiophenes with long side chains, methylene sulphides with numerous or long side chains, or simple ring methylene sulphides. Either class of formulas will satisfy the results of analysis. For example,

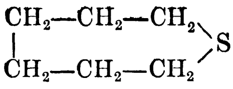


Tetra hydrothiophene or
penta methylene sulphide.

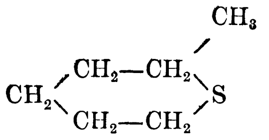


The ready formation of sulphones, addition products with alkyl iodides, and hydrates, is unlike the thiophenes, but the hydrothiophenes may behave differently. It is improbable that rings with a very large number of carbon atoms can exist. A condensed ring structure like chinoline or naptho chinoline with sulphur in place of nitrogen is excluded by the series C_nH_{2n}.

As shown above, the lowest member of the series separated from Canadian petroleum was $C_6H_{12}S$, boiling point 45°–50°, 50mm., which may be hexamethylene sulphide, or methylpentamethylene sulphide. Higher homologues may reasonably be considered as side chain derivatives: —



Hexamethylene sulphide



Methylpentamethylene sulphide

The structure of these bodies will doubtless have to be referred to the methylene ring, yet the precise form of the ring with reference to the number of carbon atoms it contains is still uncertain. For instance, the central group may be a penta-, hexa-, or hepta-methylene ring. It has therefore seemed advisable to adopt a comprehensive name that shall include any possible arrangement, and the term thiophane has been adopted. Without doubt, the structure of these sulphur derivatives will be defined with greater precision when the structure of the hydrocarbons of the series C_nH_{2n}, C_nH_{2n-2}, C_nH_{2n-4}, etc., which constitute the greater part of the constituents of petroleum with high boiling points from any source, are better understood.

UNSATURATED HYDROCARBONS OF THE SERIES C_nH_{2n}.

The need of more accurate information concerning the presence of hydrocarbons of the ethylene series C_nH_{2n} in petroleum was explained in a former paper of this series. Notwithstanding persistent attempts in the numerous treatises on petroleum to show that these bodies have been identified, a critical examination of published results fails to reveal adequate proof of sufficient foundation for these statements. The statement in "Petroleum and its Products," by Redwood, that De la Rue and Mueller proved the presence in preponderating quantities of the ethylene group in Rangoon petroleum is not supported by the results nor by the conclusions of those authors. Concerning the results of Warren, Schorlemmer, and Chandler, it is not true as asserted by Redwood that those chemists found the ethylene series in Pennsylvania petroleum. There are no allusions to this series in Schorlemmer's published papers.

Beyond adopting the general nomenclature then accepted for the ethylene series, Warren evidently left it an open question as to what should be the structural formulae of the products he separated from Pennsylvania petroleum. There are no statements in his papers to show that he made any further preparation of his products for analysis than boiling with sodium, and no further examination to prove structural forms. Certainly it would have been easy to demonstrate the unsaturated condition of those bodies had they contained double bonded carbon, and in view of Warren's clear-sighted and painstaking methods, he could not have overlooked the importance of those tests. In none of his papers on Pennsylvania petroleum does the term olefine or ethylene appear.

The assertion of Hoefer that members of the olefine series, C_2H_4 to $C_{30}H_{60}$ have been found in American petroleum has no foundation. In fact, beside the investigations within recent years in this laboratory leading to a better knowledge of the various series of hydrocarbons with high boiling points, no attempts have been made to discover the true composition of American petroleum. In fractions below 200° from Galician oil, Lachowicz obtained no reaction with bromine, yet so far as they have been examined in this laboratory, distillates below 200° from American oils do not fail to show a considerable bromine absorption. The sulphur compounds in Ohio and Canadian oils have a great affinity for bromine. Substitution may take place in the aromatic hydrocarbons which American oils contain, as well as in the hydrocarbons C_nH_{2n+2}, unless light is excluded. All these bodies, and probably others, are affected in the ordinary determinations of bromine absorption.

At the suggestion of one of us (C. F. M.), in connection with another line of work on petroleum, Mr. T. A. Hicks, a student in this laboratory, undertook a study of bromine absorption in crude oil and in fractions obtained from it after various modes of treatment. Two determinations in the oil before treatment gave as the percentage of bromine absorbed, (I), 8.43, and (II), 8.73. A portion agitated with alcoholic mercuric chloride, washed and dried, gave (I), 9.27, and (II), 9.38, indicating that the crude oil holds in solution to some extent the mercuric chloride compound. After treatment with mercuric chloride, a portion of the oil shaken with common concentrated sulphuric acid gave with bromine, (I), 5.91, and (II), 5.94. The oil was next shaken with fuming sulphuric acid, washed, and dried, when it absorbed bromine equivalent to (I), 3.47, and (II), 3.72. A portion of the oil after the last treatment was distilled under atmospheric pressure, fractions collected at 100°–125°, 125°–200°, and 200°–230°. In the first distillate the bromine absorption was, (I), 4.65, (II), 4.75, in the second, (I), 4.63, (II), 4.58, and in the third, (I), 5.61, (II), 5.17 per cent. Another portion of the treated oil was distilled in vacuo under 50 mm., collecting at 130°–160°, 160°–190°, 190°–260°, and a residue, and bromine absorption determined. Bromine absorption gave in the first distillate, (I), 1.73, (II), 2.00; in the second, (I), 1.96, (II), 2.01; in the third, (I), 3.28, (II), 3.15, and in the residue, 9.52. From these results it is evident that substitution in the less volatile portions of the crude oil or cracking has much to do with the amount of bromine absorbed, especially since in these experiments the reagents employed for the removal of the sulphur compounds should also remove unsaturated hydrocarbons. In this connection Mr. Hicks determined bromine absorption in some distillates from Pennsylvania, Ohio, and Canadian oils, that had been especially purified by long distillation and treatment with reagents, as has been more fully described in another paper. A distillate 194°–196° from Pennsylvania petroleum gave 0.02 per cent bromine absorbed; another 209°–210°, 0.09 per cent; a distillate 209°–210° Ohio purified in the same manner gave 0.03 per cent bromine, and a Canadian distillate, 0.12 per cent. These results may be accepted as showing no absorption of bromine, since this method is not capable of indicating such small percentages. That the quantity of sulphur remaining in the crude oil after treating with fuming sulphuric acid was too small to affect the amount of bromine absorbed is shown by the low percentage of sulphur, 0.09, and in the distillate 200–230 atmospheric pressure, 0.001 per cent.

When the complex composition of American petroleum is borne in mind, and the probability of substitution in the less volatile portions, the difficulties in testing for unsaturated hydrocarbons are evident. Consequently all discussion of this subject by those best informed has been undertaken with reservation, while those of others partake more of the nature of speculation on results which the authors were content merely with presenting, without attempting explanations which the facts were insufficient to justify.

We have had good evidence that unsaturated hydrocarbons are contained in distillates prepared from crude petroleum. Polymerization on standing, the formation of dark colored heavy oils, can only be explained by changes in unsaturated hydrocarbons or unsaturated sulphides. Heptylene was described in another paper as a constituent of Ohio oil.

Since the products described in this paper were contained in the oil extracted with sulphuric acid from burning oil distillate, we have assured ourselves by experiments already described that ordinary concentrated sulphuric acid such as is used in refining burning oil distillates, removes without decomposition, from such distillates, the unsaturated hydrocarbons as well as the sulphur compounds; and consequently that the sludge oil after carefully separating from the acid contained constituents of the crude oil and not products of decomposition.

In fractioning in vacuo as previously explained, a considerable proportion of the distillates from the sludge oil collected below 100°, which could be distilled without decomposition under atmospheric pressure. These portions were therefore carried through ten distillations under atmospheric pressure, and the portions distilling below 150° in vacuo also through ten additional separations in vacuo. On account of great pressure of other work, these distillates stood three years before their study was resumed, although when first obtained they received sufficient attention to show that they contained unsaturated hydrocarbons (Am. Chem. Journ., **16**, 92).

Upon returning to these distillates, it was found that some of them had undergone a marked change. Those collected at certain temperatures, — especially at 44°–45°, seventh distillation, 50 mm.; 70°–71°, twenty-second distillation, atmospheric pressure; 97°–98°, tenth distillation, atmospheric pressure; 118°–119°, tenth distillation, atmospheric pressure, — corresponding in part to the boiling points of well-known hydrocarbons of the ethylene series C_nH_{2n}, had deposited in considerable quantities heavy dark red oils, evidently products of polymerization. Some of the polymerized oils were found to contain as much as 8 per cent of sulphur, although polymerization took place in oils containing not more than 1.5 per cent of sulphur. It was interesting to observe that distillates on either side of those from which the heavy oils separated remained unchanged and were scarcely more discolored than when they were first distilled. That the distillates below 150° contain sulphur compounds with a peculiar odor, attacking the eyes and in other respects different from the series $C_nH_{2n}S$ described above, has been apparent since the first distillation of these oils, although these peculiar compounds are evidently present in much smaller proportions than the others.

All these fractions, as well as those above 150°, united with bromine with explosive violence, and with the evolution of great heat. The bromine addition products, however, were found to be so unstable that it was impossible to purify them by distillation even in vacuo. They decomposed rapidly even on standing with the separation of hydrobromic acid. In ascertaining the composition of these hydrocarbons we have, therefore, relied on the more stable addition product obtained with hydrobromic acid, which had the further advantage that, having no action on the sulphur compounds, the latter need not be removed before heating with the acid.

HEXYLENE.

For the identification of hexylene, the small quantity of the fractions 70°–80°, twenty-second distillation, atmospheric pressure, were put together, and a portion was heated to 120° during five hours with fuming hydrobromic acid. The product was washed, dried, and fractioned in vacuo. On account of the higher boiling point of the bromide it was easy to separate the addition product, and of the small quantity obtained, the greater portion collected at 62°–65°, 50 mm. The boiling point of the bromide under atmospheric pressure could not be determined on account of its instability, but it probably was not far from 135°. The distillate selected for the formation of this bromide was nearly the same in boiling point as that of the hexylenes from various sources, 65°–70°. Upon analysis values were obtained corresponding to those required for monobromhexane;

I. 0.1938 gram of the oil gave 0.3108 gram CO_2, and 0.1283 gram H_2O.
II. 0.2720 gram of the oil gave 0.3045 gram AgBr.

	Required for $C_6H_{13}Br$.	Found.	
		I.	II.
C	43.63	48.73	
H	7.88	7.41	
Br	48.51		47.64

On account of the small amount of this substance it was not possible to purify it more completely.

HEPTYLENE.

The fractions 98°–102°, tenth distillation, atmospheric pressure, more nearly corresponding to the boiling points of the various heptylenes, 90°–100°, were selected more especially because they contained a considerable quantity of the polymerized oil. On either side of these limits the distillates had not changed. After treatment with fuming hydrobromic acid and fractioning in vacuo, the greater portion of the bromide collected at 76°–80°, 50mm. It could not be distilled under atmospheric pressure, but its boiling point was probably not far from 160°. The results of analysis corresponded to the composition of monobromheptane:

I. 0.2000 gram of the oil gave 0.3498 gram CO_2, and 0.1592 gram H_2O.
II. 0.2117 gram of the oil gave 0.2188 gram AgBr.

	Required for $C_7H_{15}Br$.	Found.	
		I.	II.
C	46.97	47.71	
H	8.38	8.90	
Br	44.73	43.99	

The specific gravity of this heptyl bromide was found to be 1.1601.

OCTYLENE.

Octylene was sought for in the fraction 118°–119°, tenth distillation, atmospheric pressure, from which had separated a small quantity of the heavy polymerized oil. After heating with concentrated hydrobromic acid, the oil was fractioned in vacuo until 15 grams collected at 93°–95°, 50mm., corresponding approximately to 180°, atmospheric pressure. The boiling point of the distillate selected is near that of diisopropyl ethylene, 116°–120°, and also that of the octylene, 115°–117°, prepared from octyl chloride by Schorlemmer.

Analyses of the bromide gave values required for monobromoctane:

I. 0.1941 gram of the oil gave 0.3486 gram CO_2, and 0.1613 gram H_2O.
II. 0.1885 gram of the oil gave 0.1851 gram AgBr.

	Required for $C_8H_{17}Br$.	Found.	
		I.	II.
C	49.74	49.00	
H	8.81	9.23	
Br	41.45		41.83

The specific gravity of this octyl bromide was found to be 1.1836.

NONYLENE.

The fraction 140°–141°, tenth distillation, atmospheric pressure, was selected for the addition of hydrobromic acid. In fractioning the bromide in vacuo, after the separation of the portion not affected by the acid, the temperature rapidly rose to 110°, and more of the distillate collected at 110°–113° than at any other point in this vicinity. This product was less stable than the lower homologues, but its boiling point under atmospheric pressure would probably be in the vicinity of 200°. Upon analysis it gave values required for bromnonane:

I. 0.1798 gram of the oil gave 0.3481 gram CO_2, and 0.1501 gram H_2O.
II. 0.2117 gram of the oil gave 0.1888 gram AgBr.

	Required for $C_9H_{19}Br$.	Found.	
		I.	II.
C	52.17	52.80	
H	9.18	9.33	
Br	38.65		37.96

The specific gravity of this bromnonane was 1.2084.

Higher fractions failed to give us addition products with hydrobromic acid, either because the additive power of the hydrocarbon was too weak, or because if the addition product were formed it was decomposed by distillation in vacuum. The first explanation is probably correct, since we have never noticed the evolution of hydrobromic acid in any considerable quantity. Perhaps it is more reasonable to assume that our distillates contained no higher homologues of this series than those that were identified.

With reference to the solvent power of sulphuric acid for the hydrocarbons described above it is doubtless true that compounds with this acid of the hydrocarbons with high molecular weights are less stable and partake more of the nature of mechanical solutions. It is doubtless true also that the mechanical solvent power of the acid is increased by the other oils that the acid dissolves. If the acid solution separated from the oil be neutralized with calcium hydrate, certain lime salts are formed crystallizing in long needles, and consisting at least in part of nitrogen bases. But sulphonates of the ethylene hydrocarbons and of allied series have not been observed. That unsaturated hydrocarbons may be extracted by sulphuric acid and precipitated by dilution, has been shown in several experiments. We diluted a carboy of sludge acid by pouring slowly into water, and found the precipitated oils to contain these hydrocarbons. As to their relative proportion in the crude oil we have no precise data, but in comparison with the principal constituents it is extremely small.

Since the sulphur compounds described in this paper, as well as the alkyl sulphides, are also readily soluble in sulphuric acid, they should be removed as a part of sludge in refining burning oil distillates.

The results described in this paper may be summarized as follows: The separation from Canadian petroleum of the following series of sulphur compounds: hexyl, heptyl, octyl, nonyl, decyl, undecyl, quartdecyl, sexdecyl, octodecyl thiophanes; the formation of corresponding sulphones by oxidation.

Canadian petroleum contains in minute proportions unsaturated hydrocarbons C_nH_{2n} apparently of the ethylene series. Canadian petroleum contains certain sulphur-free oils soluble in alcohol and different in odor and in other respects from the series hitherto identified in petroleum, possibly terpenes.

We desire to acknowledge our obligations to Messrs. C. A. Lattimer and R. C. McBride, for assistance in the purification and analysis of the sulphur compounds.